STRUCTURAL AND MECHANICAL EFFECTS OF INTERSTITIAL SINKS

by

Mark J. Klein

January 1969

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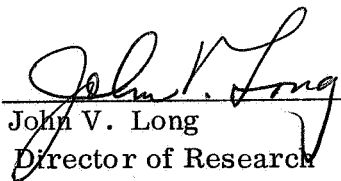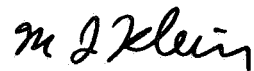
ABSTRACT

The contribution of solutes to the creep strength of columbium-base and tantalum-base alloys is being studied through their effect on the activation energy for creep, H. Near $0.5\,T_M$, H for unalloyed columbium was found to be a sensitive function of the structure and interstitial concentration. For a constant interstitial concentration H may approach a constant value as the structure approaches a stable configuration. Activation-energy temperature profiles were determined over the temperature range 1800 to 2800°F for the columbium-base alloys Cb-1Zr, C-129Y and C-103. The results obtained thus far indicate that H for these alloys is constant or decreases slightly with increasing temperature. Near 2800°F, however, H for C-129Y and C-103 increases with increasing temperature.

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INTRODUCTION

This is the eighth quarterly progress report for the Contract NAS-7-469, "Structural Effects of Interstitial Sinks," covering the period September 8 through December 8, 1968.

The first part of this program was primarily concerned with the change in structure, strength, and interstitial concentration in a refractory alloy induced by an interstitial sink. The loss of carbon from D43 (a columbium-base alloy strengthened with a carbide dispersion) to a titanium sink was correlated with the creep behavior of the D43. The creep rate near $0.5 T_M$ was found to be proportional to the carbon lost to the interstitial sink.

In subsequent work the scope of the program was broadened to include the effect of interstitial and substitutional solutes on the creep of columbium and tantalum-base alloys. Since creep is thermally activated, the creep rate and, therefore, the creep strength is a sensitive function of the magnitude of the activation energy for creep. Therefore, the influence of solutes on creep strength is being studied through their effect on this parameter. This phase of the investigation should provide information concerning the role that various solutes play in strengthening refractory alloys — information of value in selecting solutes to optimize the high temperature strength of refractory alloys.

In past work anomalous increases in the activation energies for creep of D43 and columbium were detected near $0.5 T_M$. These increases in the activation energies were found to be a function of the interstitial concentration of these metals. During this period the factors affecting the activation energy for creep of columbium were investigated further. In addition, the activation-energy temperature profiles were determined for three columbium-base alloys over the temperature range 1800 to 2800°F.

The experimental procedures used in this investigation have been reported in the interim report covering the period 8 June, 1966 through 8 June, 1967. Therefore, experimental procedures will be discussed in this report only when new techniques are involved.

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RESULTS AND DISCUSSION

In this section data are presented showing the change in the apparent activation energy for creep, H, for columbium and the columbium-base alloys, Cb-1Zr, C-129Y and C-103, over the temperature range 0.4 to $0.65\,T_M$. The results for columbium are presented first since these data form a basis to compare the values of H for the columbium-base alloys.

Activation energies were determined using the temperature shift method previously described (Interim Tech. Rept. June 1966 – June 1967). The temperature was ordinarily shifted 100°F during constant stress creep tests and the value of H reported is that for the mean temperature.

2.1 ACTIVATION ENERGIES FOR CREEP OF COLUMBIUM

During the last period the activation energy for creep of columbium was determined from about 0.4 to $0.65\,T_M$. Specimens whose gage lengths were wrapped with tungsten foil to minimize contamination by gaseous interstitials during heat treating and testing yielded lower values of H than specimens exposed directly to the vacuum (10^{-6} Torr) (compare solid line profiles in Fig. 1 for Lot 1 Cb). It was concluded that interstitial contamination during testing increased the value of H. During this period several tests were performed to give additional information concerning the effect of structure and interstitial concentration on the value of H near $0.5\,T_M$.

2.1.1 The Effect of Interstitials on the Activation Energy

The concentration of interstitials in columbium creep specimens was varied by heat treating and testing specimens wrapped with tungsten foil and specimens exposed to the vacuum. It has been shown that the foil reduces impingement by gaseous interstitials during vacuum heat treatments and thus reduces contamination of the specimen with interstitials [1]. Therefore, wrapped and unwrapped specimens given the same heat treatment will have the same structure but different interstitial concentrations. The effects of wrapping the specimens and heat treating them on the activation energy for creep at 1850°F are listed in Table I. Most of the specimens were given a precreep heat treatment at 2300°F; the intended purpose of this treatment was to stabilize the grain structure for creep testing at lower temperatures.

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(1) F. F. Schmidt, D. J. Maykuth, and H. R. Ogden, DMIC Rept. 205, 1964.
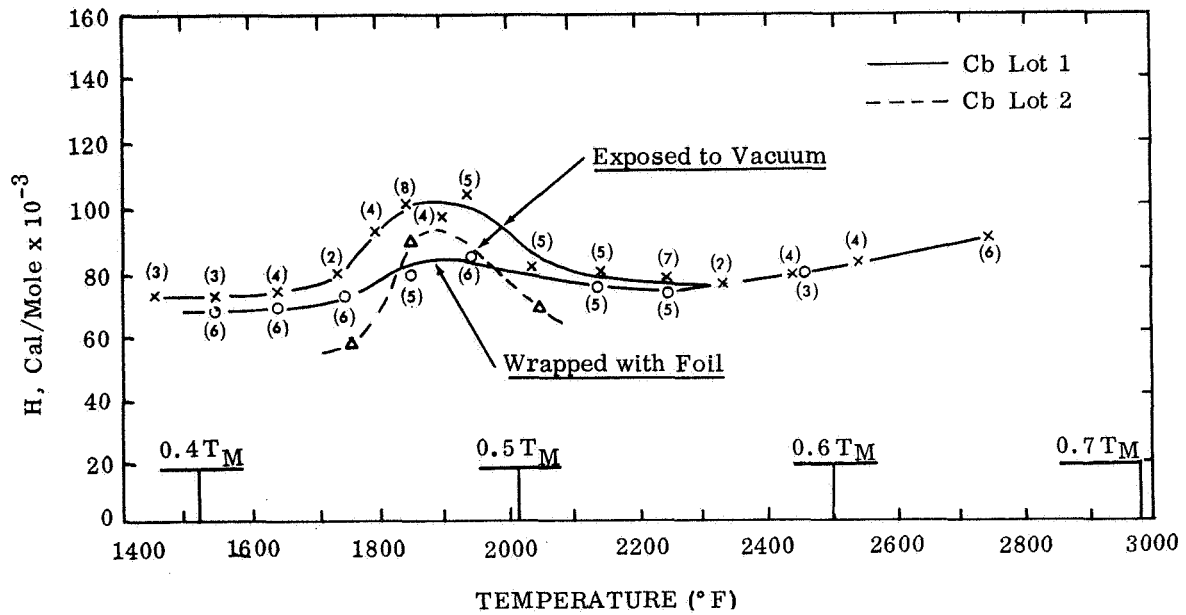
Figure 1. The Activation Energy for Creep over a Range of Temperature for Two Test Lots of Columbium

TABLE I

Variation in H for Cb at 1850°F with Precreep Treatment and Test Conditions

SPECIMEN NO.	PRECREEP TREATMENT	TEST CONDITIONS	H (Cal/mole x 10^{-3})
1	2300°F/5 min. (not wrapped)	Not Wrapped	102
2	2300°F/5 min. (wrapped)	Wrapped	79
3	2300°F/1 hour (not wrapped)	Not Wrapped	150
4	2300°F/1 hour (wrapped)	Wrapped	115
5	As Received	Not Wrapped	68
6	As Received	Wrapped	65
7	2300°F/5 min. (wrapped)	Not Wrapped Vacuum of 10^{-5} Torr.	100
1A	2300°F/5 min. (not wrapped)	Not Wrapped	91
2A	2300°F/5 min. (wrapped)	Wrapped	75

Specimens numbered 1 through 7 were obtained from columbium (Lot 1) containing 200 ppm oxygen and 95 ppm nitrogen and specimens 1A and 2A were obtained from columbium (Lot 2) containing 85 ppm oxygen and 110 ppm nitrogen in the as-received conditions. Both lots of columbium contained Cr and Cu as the major substitutional impurities (in concentrations <0.1%). Past work[1] has shown that the major interstitial contaminants introduced during vacuum heat treatments of columbium and columbium alloys are oxygen and nitrogen. Analyses of some of the wrapped and unwrapped specimens showed that the wrapped specimens were lower in these interstitials than the unwrapped specimens but the analyses were not sufficiently accurate to yield quantitative differences in interstitial concentrations.

As shown in Table I, all of the wrapped specimens yield lower values of H than the unwrapped specimens for identical precreep treatments. This suggests that interstitial contamination increases the value of H at the peak in activation energy values near 1900° F. The specimens tested directly without a precreep heat treatment (5 and 6) yield about the same values of H for both the wrapped and unwrapped conditions indicating that the interstitial contamination affecting H takes place primarily during the 2300° F heat treatment rather than during creep testing at 1800-1900° F. However, the results suggest that sufficient interstitial contamination to increase H may occur at 1800-1900° F if the specimens are tested in a vacuum of 10^{-5} Torr (Spec. #7).

The activation energies from Table I are shown plotted as a function of the annealing time at 2300° F in Figure 2. Curves connecting the data for the wrapped
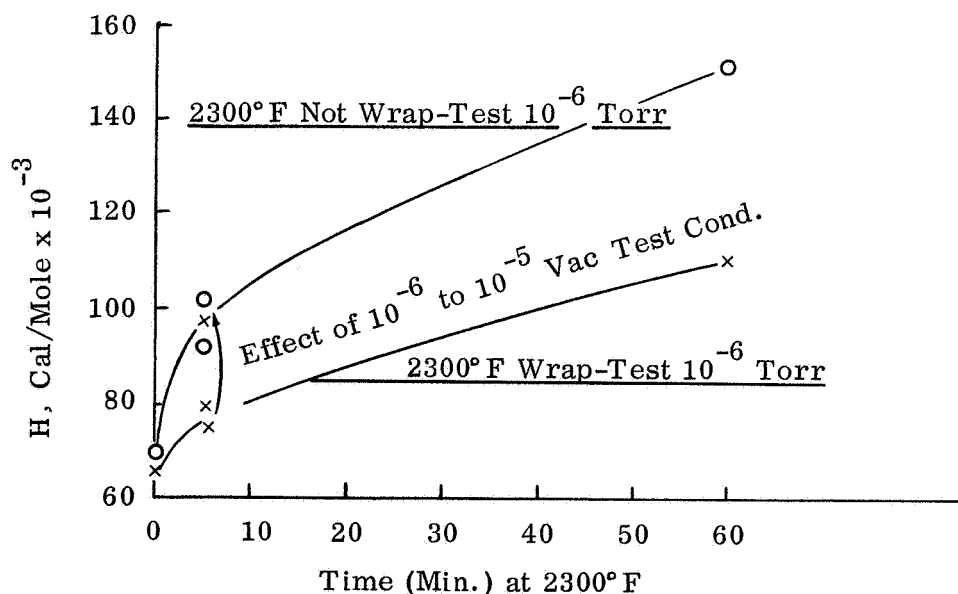

Figure 2. Data of Table I Showing Effect of Annealing Wrapped and Unwrapped Specimens at 2300° F on the Value of H at 1850° F

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and unwrapped specimens show the effect of interstitial contamination on H. The effect of testing in a vacuum of 10^{-5} Torr (Spec. 7) rather than the normal vacuum of 10^{-6} Torr on the value of H is also indicated in this figure.

The sensitivity of H to the interstitial concentration is also suggested from a comparison of the values of H derived from columbium with different initial interstitial concentrations. Specimen 1A and 2A (85 ppm O and 110 ppm N) yield lower values of H than specimens 1 and 2 (200 ppm O and 95 ppm N). Additional values of H for the columbium with the lower initial oxygen concentration are shown in Figure 1, (dashed line). These data suggest that there is also a peak in the activation energy temperature profile for this lot of columbium and that it occurs at about the same temperature (1800-2000°F). However, the peak for the columbium lower in initial oxygen (dashed line) appears to be somewhat larger and to occur at a lower value of H than that for the columbium higher in oxygen (solid line) when both are exposed to the vacuum.

A comparison of the values H for the wrapped and unwrapped specimens given the same heat treatment certainly suggests that the interstitial concentration affects the value of H near $0.5\,T_M$ for unalloyed columbium. However, evidence was obtained indicating that other factors may also affect H for columbium near this temperature. This is shown by the following test. The interstitial concentration in a specimen was increased to 3000 ppm oxygen and 135 ppm nitrogen. The value of H at 1850°F for this specimen was about the same as that for a specimen with only 135 ppm oxygen and 95 ppm nitrogen (i.e., $100 \times 10^{+3}$ cal/mole). Evidently there is a limit to the increase in H that can be induced simply by increasing the interstitial concentration. Therefore, other factors such as the ratio of interstitials to dislocations or to impurity solutes must also affect H if values exceeding $100 \times 10^{+3}$ cal/mole are to be accounted for (e.g., Spec. 3 and 4, Table I). In the following paragraphs the results of a series of tests performed to sort out the effect of structure on H are presented.

2.1.2 Effect of Structure on the Activation Energy

One way to determine the effect of structure on H is to determine the activation energy as a function of strain during primary creep at a temperature where interstitial contamination is not a problem. During primary creep the creep rate decreases because the structure becomes progressively more worked. Therefore, if H varies with strain during primary creep it also varies with structure. The duration of primary creep above about $0.5\,T_M$ is ordinarily too short to determine the activation energy as a function of strain using the temperature shift method. However, below $0.5\,T_M$ primary creep (P) becomes more extensive until it can comprise the entire creep curve, and in this event the creep rate will continue to decrease until creep can no longer be detected (see adjacent sketch).

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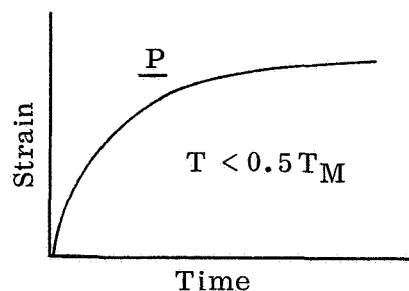
H is shown as a function of strain in Figure 3 for specimens tested at three different temperatures after they were annealed at 2300° F. Activation energies were determined for the specimen tested at 1850° F and 1550° F during approximately steady state creep conditions (i.e., constant structure), whereas, primary creep continued throughout most of the test at 1275° F, implying a continuous variation of structure. The test at 1275° F shows that H is a function of structure since the structure is the only variable during this test. H is initially very high at low strain when the annealed specimen is initially tested at 1275° F and H decreases as the specimen becomes more worked with increasing creep strain. Apparently the value of H decreases until the structure attains an equilibrium configuration for the test conditions at about 14 percent strain. The data at 1550° F also show the same trend toward decreasing values of H with increasing strain.

Previous results show that interstitial contamination during creep testing is not sufficient to affect H at 1850° F in a vacuum of 10^{-6} Torr. Therefore, interstitial contamination during creep testing is not likely to be a factor affecting the activation energy values shown in Figure 3.

The effect of structure on the magnitude of H was tested further by determining the activation energy for specimens given different precreep treatments. The activation energy was measured at 1275° F for two specimens. The first specimen was tested after it was annealed 5 min at 2300° F. The second specimen was given the same precreep heat treatment and then it was strained 10 percent in the temperature range 1500 to 1600° F before its activation energy was measured at 1275° F. The variation in activation energy with creep strain for these specimens is shown in Figure 4. The results show that the difference in precreep treatments and, therefore, the difference in initial structure affects the activation energy for creep at 1275° F. However, the difference in the values of H for the two specimens diminishes as the creep strain increases. The activation energies for both specimens approach asymptotic values at about 14 percent strain that do not differ greatly. Apparently the values of H will be approximately the same when the equilibrium creep structure for creep at 1275° F is attained.

As shown in Figure 5, the activation energy for creep at 2150° F is also a sensitive function of the thermal and mechanical history of the columbium specimens. The activation energy for creep for specimen A was measured at 2150° F after it was first annealed 5 minutes at 2300° F. Specimen B was crept to 10 percent strain in the temperature region 2500-2600° F and then H was measured at 2150° F. These different precreep treatments have drastically altered the value of H at 2150° F. The activation energy for creep for specimen B is about twice that for specimen A at the same strain. However, the values of H for both specimens could approach the same value if creep could be continued to sufficiently high strains. The structure of specimen B may require extensive creep deformation at 2300° F before it attains an equilibrium creep structure.
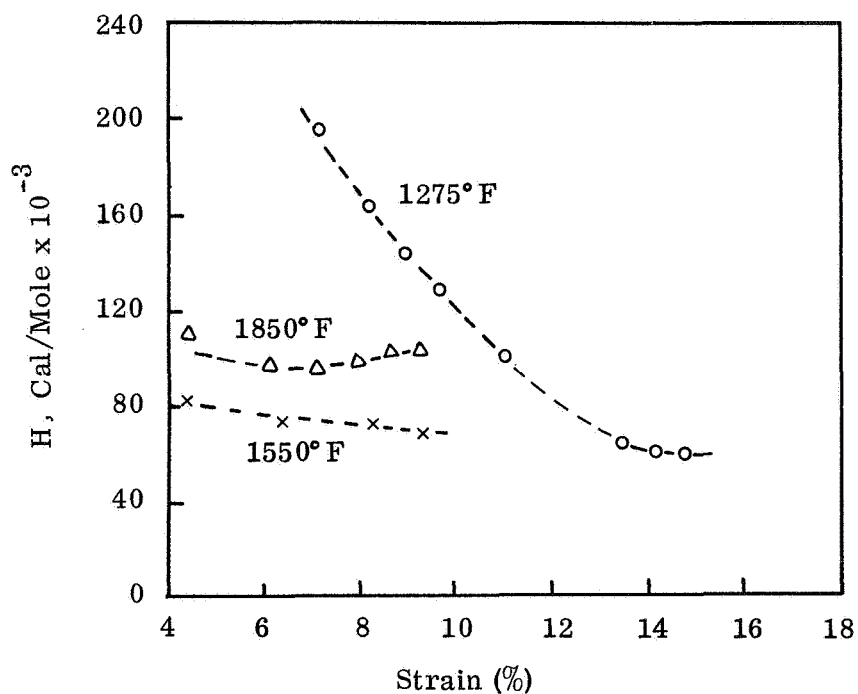
Figure 3. Activation Energy for Creep versus Strain at 1850°F, 1550°F and 1275°F
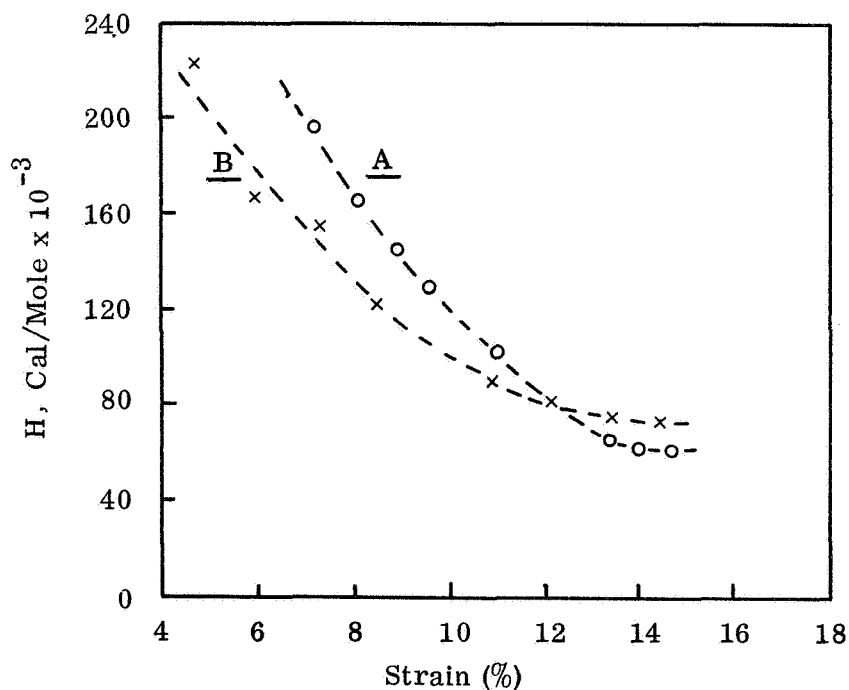(Precreep treatment 2300°F/ 5 min)

Figure 4. Activation Energy for Creep versus Strain at 1275°F for Specimens Given
Different Precreep Treatments. (Specimen A 2300/5 min, Specimen B
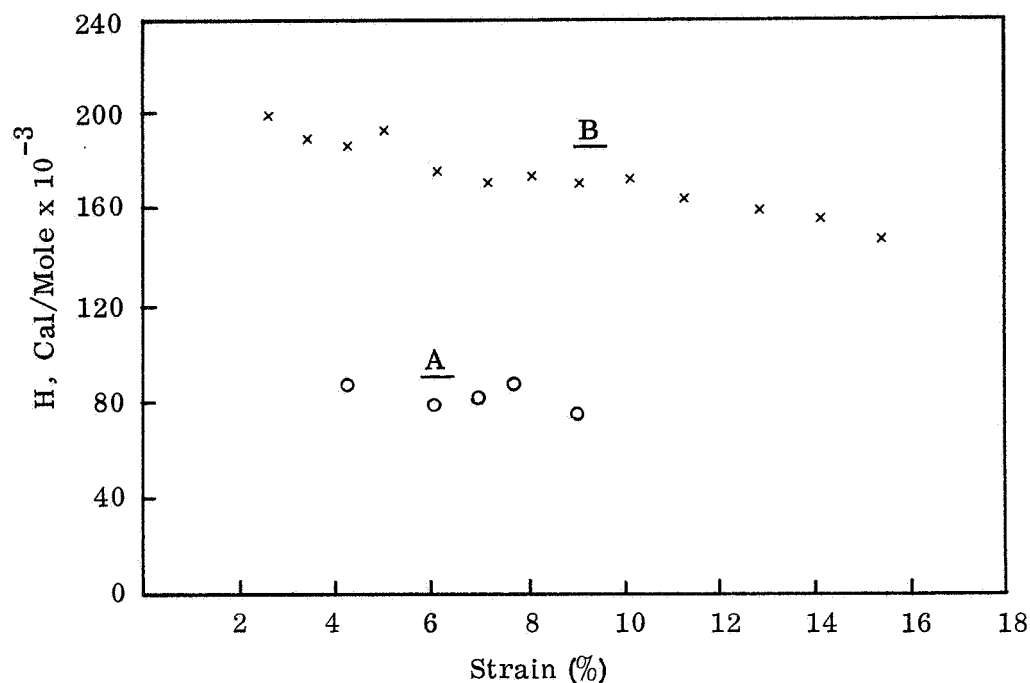2300/5 min, and crept at 1500-1600°F to 10% strain)

Figure 5.   Activation Energy as a Function of Strain at 2150°F for Specimens Given
Different Precreep Treatments (Spec. A, 2300/5min; Spec. B, Crept
2500-2600°F to 10% Strain)

In the previous section (2.1.1) it was shown that H near $0.5\,T_M$ is a function
of the interstitial concentration of the columbium specimens. The tests described in
this section show that H is also a function of the initial structure of the columbium
and the structural changes occurring during creep. However, the results suggest that
H may reach a constant value when the structure attains an equilibrium configuration
for the test conditions. This hypothesis will be investigated further in future work.

## 2.2   ACTIVATION ENERGY FOR CREEP OF COLUMBIUM ALLOYS

Activation energies were determined as a function of strain and temperature for
the three columbium-base alloys Cb1Zr, C103 (Cb-10Hf-1Ti-0.5Zr) and C-129Y (Cb-
10W-10Hf-0.1Y). The grain structure of the alloys in the as-received condition are
shown in Figure 6 and their interstitial concentrations are listed in Table II. Specimens
tested below 2800°F were wrapped with foil, as previously described, to minimize
interstitial contamination during testing. Specimens tested at 2800°F were not wrapped
because sticking of the foil to the gage length of the specimen interferred with creep
measurements. In this regard, the results for D43 suggest that changes in interstitial
concentration that may occur during testing do not affect H in this temperature range
(Seventh Quarterly Report, October, 1968).

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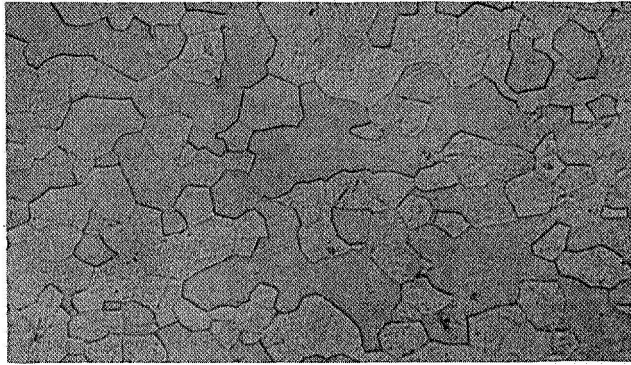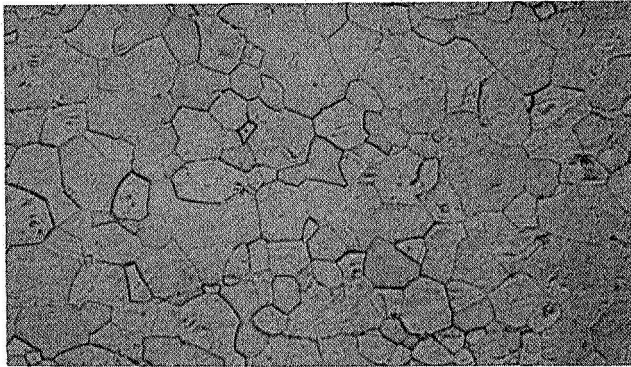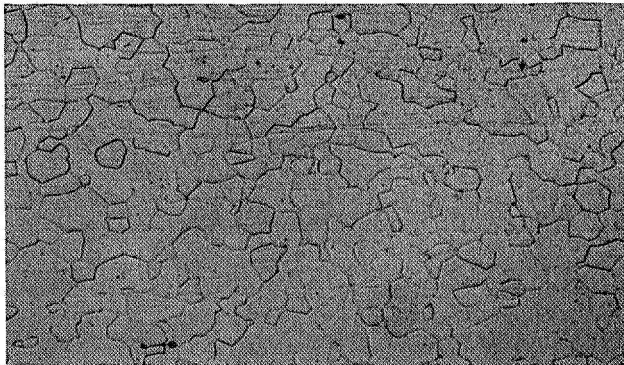
Cb-1Zr

C-103

C-129Y

Figure 6.   Structure of As-Received Columbium-Base Alloys
            (Magnification 250X)

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TABLE II
INTERSTITIAL CONCENTRATIONS IN COLUMBIUM ALLOYS

Alloy	INTERSTITIAL CONCENTRATIONS (ppm)			
	C	H	O	N
Cb-1Zr	44	<5	325	60
C-103	80	5	205	95
C-129Y	60	<5	110	18

Most of the activation energy measurements were made over a range of strain using a constant stress throughout the test. However, in some cases the stress was changed during the test to keep the strain rate at a convenient level. These changes in stress did not noticeably affect the activation energies derived from these tests (Fig. 7).

The activation energies for these alloys were ordinarily approximately independent of creep strain (Figures 8-10). However, some exceptions were noted. At 1850°F the activation energy for creep of the alloys showed a tendency to decrease with increasing strain (Fig. 8). This was especially noticeable for Cb-1Zr. In addition, at 2650°F there was a tendency for the activation energy for creep of C-103 and C-129Y to increase with increasing creep strain (Fig. 10). Activation energy measurements for these alloys were ordinarily made in regions of approximately steady
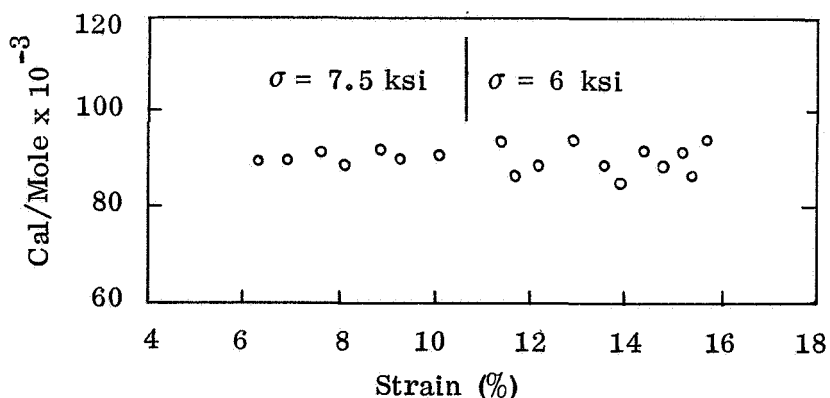

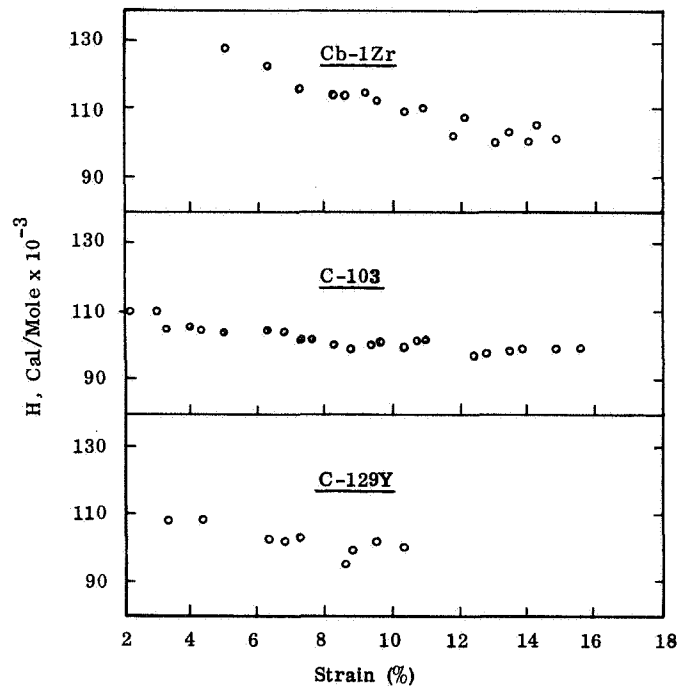Figure 7.   Activation Energy for C-103 at 2350°F at Different Stress

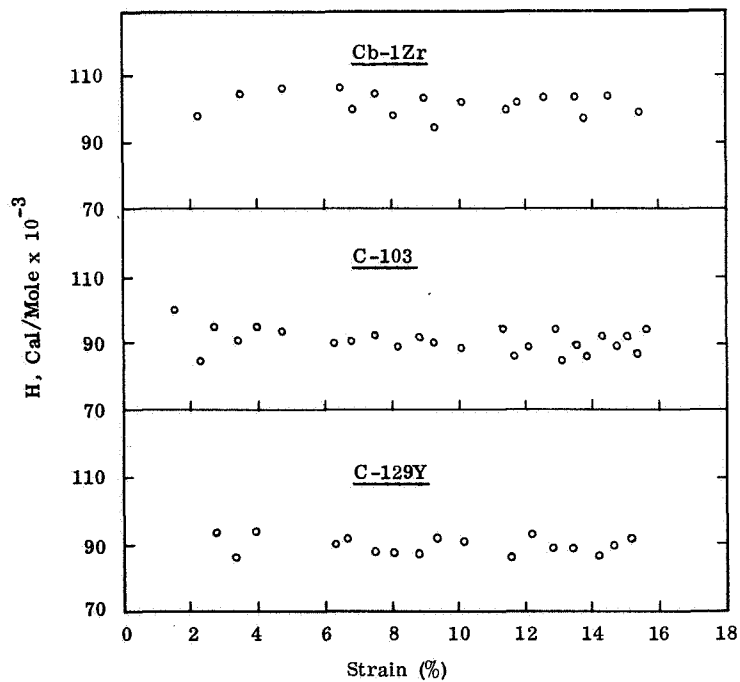Figure 8. Activation Energy as a Function of Strain at 1850° F for Three Columbium-Base Alloys

Figure 9. Activation Energy as a Function of Strain at 2350° F for Three Columbium-Base Alloys
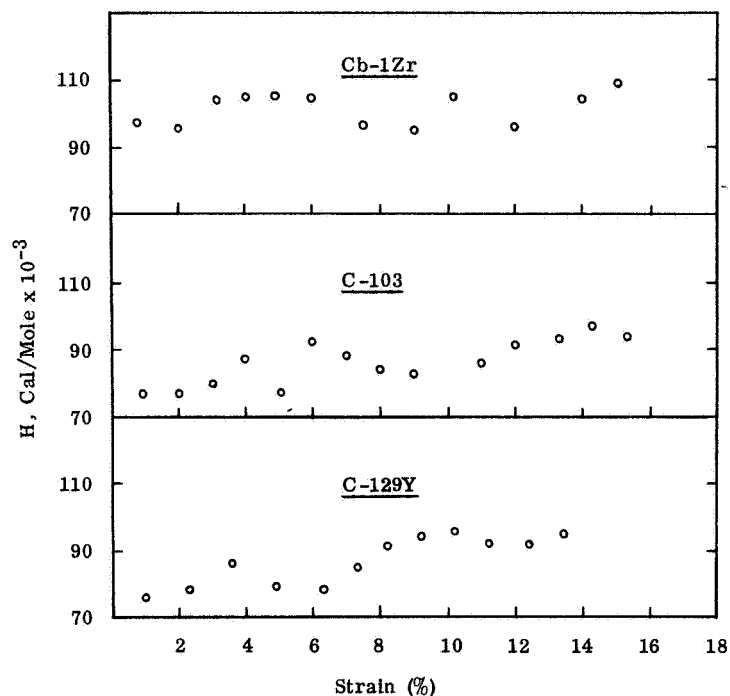
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Figure 10.   Activation Energy as A Function of Strain at 2650° F for Three Columbium-
             Base Alloys

state creep. However, the creep rate for these alloys did not attain a true steady
state condition over the entire range of strain tested. This is believed to be caused
by structural changes that occur during creep such as solutioning, precipitation or
overaging of dispersions in the alloys that may induce changes in the dislocation or
grain structure during creep testing. In view of the sensitivity of H to the structure
of columbium found previously, the variation in H with strain for the alloys may be
caused by structural changes that occur during creep. On this basis, as the structure
approaches a stable configuration at high strains or during prolonged testing, H may
approach a constant value.

The activation energies are shown in Figure 11 over a range of temperatures
for the three alloys. The data plotted in this figure are the average values of H for
the first 10 to 15 percent creep strain. Since H is somewhat dependent upon strain,
the data shown in Figure 11 would be different if the values of H were compared at a
specific strain or at a strain where the structure has attained an equilibrium configur-
ation. However, the relative values for the different alloys would be about the same
and the absolute values would only vary slightly from the average values shown in this
figure. For comparison, the activation energy/temperature profiles obtained previously
for D43 (Cb-10W-1Zr-0.1C) and Cb (sheathed specimens) are also shown (dashed lines)
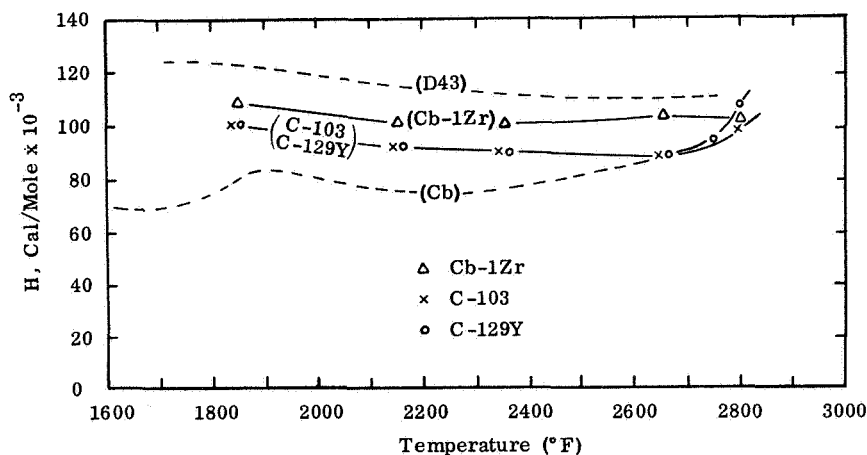in this figure.

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Figure 11. The Activation Energy for Creep of Columbium and Some Columbium
Alloys Over a Range of Temperatures

D43 has the highest activation energy in the temperature range studied. However, the values of H for C-103 and C-129Y appear to be increasing with increasing temperature near 2800°F. Additional work will be required to determine if there is a significant increase in the value of H for these two alloys above 2800°F. As previously discussed, a significant increase in H is likely to be accompanied by an increase in the strength of these alloys.

The values of H for columbium are generally lower than those for the alloys in the temperature range studied. However, as previously pointed out, H for columbium is a sensitive function of the interstitial concentration and the structure in the temperature region below about 2200°F. Therefore, the data for columbium in this temperature region do not form a good basis to compare the effect that solutes in the various alloys might have on the value of H. Above about 2200°F, H for columbium appears to be approaching the value of the activation energy for self-diffusion ($\sim$97 x 10^{+3} cal/mole). Near 2700°F the values of H for C-103 and C-129Y are about the same as that for columbium. In future work the activation energy/temperature profile for columbium will be extended to higher temperatures to use as a basis of comparison with the activation energy for the various alloys.

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SUMMARY AND CONCLUSIONS

The activation energy for creep, H, was determined for columbium specimens whose gage lengths were sheathed with foil to minimize interstitial contamination during testing. H was also measured for unsheathed columbium specimens. The results of these tests show that the activation energy for creep of columbium near $0.5T_M$ is a function of its interstitial concentration (probably oxygen or nitrogen). The interstitials in columbium appear to contribute to an activation energy peak between 1800°F and 2000°F when H is determined as a function of temperature. One mechanism thought to account for activation energy peaks in other metals is an interaction between solutes (or solutes in combinations) and moving dislocations. The temperature range of the peak is probably too high to be caused by an interstitials-dislocation interaction. However, the mobility of interstitials combined with other impurity solutes in columbium may be of the correct order to account for the activation energy peak.

H for columbium near $0.5T_M$ is also a function of the structure of columbium (e.g., grain or subgrain size, dislocation density or configuration) near $0.5T_M$. This was shown by the dependence of H on precreep structure and structural changes that occur during primary creep. However, the results indicate that H may approach a constant value when an equilibrium structure is attained for the condition of the creep test.

The activation energies were determined for the columbium-base alloy Cb-1Zr, C-103 and C129Y as a function of strain at different temperatures. The activation energies for these alloys were ordinarily found to be approximately independent of creep strain, but some minor exceptions were noted at 1850 and 2650°F. Activation-energy temperature profiles were determined for these alloys in the temperature range 1800 to 2800°F. The activation energies for C-103 and C-129Y are almost the same in this temperature range. The values of H for both alloys show an increase near 2800°F.

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FUTURE WORK

The activation energy temperature profiles for columbium and the columbium alloys will be extended to higher temperatures where substitutional elements are more likely to affect the activation energy for creep and where the effect of structure and interstitials on H will tend to be less important. In addition, activation energies will be determined over a range of temperatures for the tantalum-base alloy, T-222. The results will be analyzed to sort out the influence of the various solutes on the creep strength through their effect on the activation energy for creep. This study should provide information of value in selecting solutes to optimize the high temperature strength of refractory alloys.